

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improved Process for the Preparation of Polyarylene Polyethers

We, UNION CARBIDE CORPORATION, a Corporation organised under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the preparation of polyarylene polyethers and to polymers produced thereby.

There are known one-step and two-step processes for the preparation of linear thermoplastic polyarylene polyethers composed of recurring units having the formula:



wherein E is the residuum of a dihydric phenol and E' is the residuum of a dihalobenzenoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the valence bonds, and where both of said residua are co-valently bonded to the ether oxygens through aromatic carbon atoms. In the one-step process for preparing these polymers, substantially equimolar amounts of an alkali metal double salt of a dihydric phenol and a dihalobenzenoid compound having an inert electron withdrawing group as described above are reacted in the presence of specific liquid organic sulfoxide or sulfone reaction solvents under substantially anhydrous conditions. In the two-step process, a dihydric phenol is first converted *in situ* in the sulfoxide or sulfone reaction solvent to the alkali metal salt by reacting with the alkali metal, the alkali metal hydride, alkali metal hydroxide, alkali metal alkoxide or the alkali metal alkyl compounds. Thereafter, water which is present or formed is removed to secure substantially anhydrous conditions, and the thus formed alkali metal double salt of a dihydric phenol is reacted with about stoichiometric amounts of a dihalobenzenoid compound which is added after the *in situ* conversion.

It has been found, however, with both the one-step and the two-step processes, long reaction times are needed in order to secure high molecular weight polymers. It has also been found that with either process, a polymer having poor color as is evidenced by a dark amber color, but which is otherwise unaffected, is produced. It is felt that poor polymer color is due to air contamination of the reaction mass during the sequential addition of solvents and reactants.

These and other drawbacks of the aforesaid one-step and two-step processes are overcome by the present invention. Reaction time as low as about one-half hour is all the time that is required to form a high molecular weight product whereas before undesirably long reaction times of from about 1 to about 6 hours were required. Furthermore, it is possible to obtain polymer product greatly improved in color as compared to polymer products obtained previously.

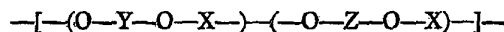
Broadly, an improved one-step process of this invention for preparing substantially linear, thermoplastic polyarylene polyethers comprises simultaneously contacting substantially equimolar amounts of an alkali metal double salt of a dihydric phenol and a dihalobenzenoid compound with a solvent mixture comprising an azeotropic former and a sulfoxide or sulfone reaction solvent in a weight ratio of from 10:1

to 1:1, preferably from 4:1 to 3:1, removing water from the reaction mass as an azeotrope with the azeotrope former until substantially anhydrous conditions are attained, adjusting the ratio of azeotrope former to reaction solvent to from 1:1 to 1:10, preferably from 1:3 to 1:4, by removing excess azeotrope former, and reacting the alkali metal double salt with the dihalobenzenoid compound in the liquid phase of the sulfoxide or sulfone reaction solvent.

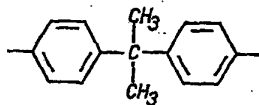
In another embodiment of this invention, polyarylene polyethers are prepared by a two-step process wherein substantially equimolar amounts of a dihydric phenol, rather than the alkali metal double salt thereof, and a dihalobenzenoid compound are simultaneously contacted with the solvent mixture as described above. The dihydric phenol is then converted *in situ* to the alkali metal double salt by reacting with about stoichiometric amounts of the alkali metal, the alkali metal hydride, alkali metal hydroxide, alkali metal alkoxide or the alkali metal alkyl compounds. Thereafter water is removed, the solvent ratio adjusted and the monomers reacted as in the one-step process described above.

In a preferred embodiment of this invention, oxygen is excluded from the reaction mass, by sparging with an inert gas e.g. nitrogen or by similar techniques, throughout the entire one-step or two-step process. It is felt that because the solvent mixture and reactants are contacted simultaneously and sparged with an inert gas, air contamination of the reaction mass is prevented and consequently a polymer of improved color is produced. Previously, air contamination of the reaction mass occurred during the sequential addition of the reactants. Blanketing the reaction mass with an inert gas did not prevent contamination because sequential addition of the reactants interrupted the inert gas "blanket".

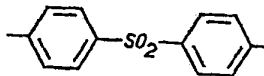
Novel polyarylene polyethers that can be prepared using the improved process of this invention are substantially linear polymers composed of recurring units having the formula



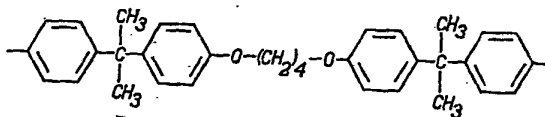
wherein: Y is



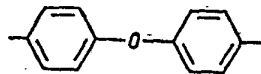
X is



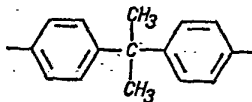
and Z is



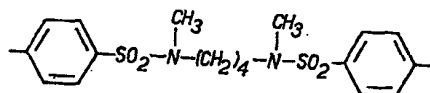
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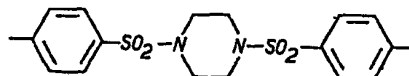
or Y and Z are the same and are



and X is

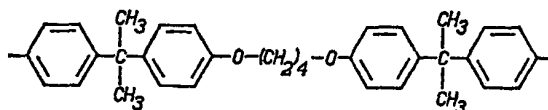


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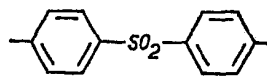
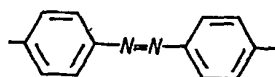


5 or Y and Z are the same and are

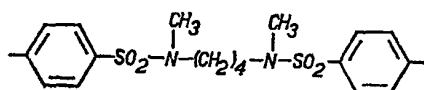
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and X is

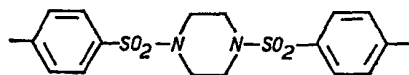


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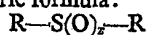
or



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The polymerization reaction proceeds without the need of a catalyst, but the use of specific sulfoxide or sulfone reaction solvents is essential to promote the reaction to a useful, high molecular weight product. The sulfoxide or sulfone reaction solvents are those having the following generic formula:

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where each R represents a monovalent hydrocarbon group free of aliphatic unsaturation on the alpha carbon atom, and contains less than 8 carbon atoms or when connected together represents a divalent alkylene group with z being 1 or 2. In all of these solvents all oxygens and two carbon atoms are bonded directly to the sulfur atom.

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Suitable solvents include dimethylsulfoxide, dimethylsulfone, diisopropylsulfone, diphenylsulfone, tetrahydrothiophene 1,1-dioxide (commonly called tetramethylene sulfone or sulfolane) and tetrahydrothiophene-1 monoxide. Dimethylsulfoxide has been found to be the most useful as the solvent for this reaction because it is a solvent for the widest variety of reactants as well as for the resulting polymer of the reaction.

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It is essential in the polymerization reaction that the reactants be maintained substantially anhydrous before and during the reaction. While amounts of water up to about one per cent can be tolerated, and are somewhat beneficial when employed with fluorinated dihalobenzenoid compounds, amounts of water substantially greater than this are desirably avoided as the reaction of water with the dihalobenzenoid compound leads to formation of phenolic species and only low molecular weight products are secured. In order to secure the high molecular weight products, the reactant should be substantially anhydrous, and preferably with less than 0.5 per cent by weight water in the reaction mass.

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In order to obtain substantially anhydrous conditions before proceeding with the polymerization reaction, water that is present or formed in the reaction mass is removed as an azeotrope with an azeotrope former. It has been found convenient to employ benzene, xylene, halogenated benzenes or other inert organic azeotrope-forming organic liquids in performing this. Heating at reflux until substantially all water present is removed as an azeotrope is the most desirable.

It is not essential that all of the azeotrope former be removed before the polymerization reaction of the alkali metal double salt of the dihydric phenol with the dihalobenzenoid compound. In fact, it is desirable to employ an amount of such material in excess of that needed to remove all of the water, as an azeotrope, with the balance being used as a cosolvent or inert diluent with the sulfone or sulfoxide reaction solvent. However, as is described below, the ratio of azeotrope former to reaction solvent must be adjusted to within certain limits before significant polymerization can occur.

The azeotrope former can be one either miscible or immiscible with the sulfone or sulfoxide reaction solvent. If it is not miscible it should be one which will not cause precipitation of the polymer in the reaction mass.

It is preferred to employ azeotrope formers which are miscible with the major solvents and which also act as cosolvents for the polymer during polymerization. Chlorobenzene, dichlorobenzene and xylene are azeotrope formers of this class. Preferably the azeotrope former should be one boiling below the decomposition temperature of the major solvent and be perfectly stable and inert in the process, particularly inert to the alkali metal hydroxide when the alkali metal salt of the dihydric phenol is prepared *in situ* in the presence of the inert diluent or azeotrope former.

Any of the alkali metal hydroxides can be employed in the two-step process; that is to say any alkali metal salt of the dihydric phenol can be used as the one reactant. The alkali metal salt should be the double metal salt. Single metal salts ordinarily limit the molecular weight of the product. The alkali metal moieties of this compound however can be the same or different alkali metals.

Substantially equimolar amounts of the alkali metal double salt of a dihydric phenol (or a dihydric phenol for *in situ* conversion to the salt) and a dihalobenzenoid compound are simultaneously contacted with a solvent mixture comprising an azeotrope former and a sulfone or sulfoxide reaction solvent in a ratio of from 10:1 to 1:1 by weight based on the combined weight of the azeotrope former and reaction solvent. It has been found that when water is present in this solvent mixture, a phase separation occurs even between normally miscible liquids creating two liquid phases. When this phase separation occurs, it has also been found that the water and hydrated alkali metal double salt of a dihydric phenol, discussed in more detail below, are preferentially dissolved in the sulfoxide or sulfone reaction solvent phase and the dihalobenzenoid compound is preferentially dissolved in the azeotrope former phase. The initial ratio of azeotrope former to reaction solvent is critical in this respect because with lesser amounts of azeotrope former, two liquid phases are not formed and undesirable hydrolysis of the dihalobenzenoid compound occurs. Only when the ratios specified are used does a phase separation occur which isolates the dihalobenzenoid compound from hydrolysis by the water in the reaction mixture.

If dry crystalline alkali metal salt of a dihydric phenol is employed, problems relative to obtaining anhydrous conditions are essentially avoided. However, drying the salt and keeping it dry during transfer and charging is extremely difficult. It has been found to be more advantageous to employ a hydrated alkali metal salt which is dehydrated in the reaction mass by removing the water of hydration. Water then can be present or formed in the reaction mass as the water of hydration of a hydrated alkali metal salt, as the water of neutralization formed during the *in situ* conversion of a dihydric phenol to the alkali metal double salt, or as water present in either the azeotrope former or the reaction solvent.

It is preferred to employ a hydrated alkali metal double salt of a dihydric phenol or to form the alkali metal salt *in situ*. During the *in situ* conversion, the hydrated salt is formed first which is then dehydrated upon the removal of water.

When the two liquid phases are formed, it is important that the water in the reaction mixture be removed as quickly as possible, usually by refluxing the mixture at about the boiling point of the azeotrope former until substantially all of the water is removed. During the water removal, the dehydrated alkali metal double salt, which is insoluble in the reaction solvent at the reflux temperatures, precipitates. The fact that all the water has been removed is usually indicated by no further precipitate formation, no further azeotrope formation, and the formation of one liquid phase when miscible liquids are used.

After the water has been removed, excess azeotrope former is removed by distillation until the ratio of azeotrope former to sulfoxide or sulfone reaction solvent is about 1:1 to 1:10. Only when the amount of azeotrope former is reduced to within these ratios, does significant polymerization occur.

5 Essentially, the reaction between the dihalobenzenoid compound and the alkali metal salt of the bisphenol proceeds on an equimolar basis. This can be slightly varied but as little a variation as 5 per cent away from equal molar amounts seriously reduces the molecular weight of the polymers. 5

10 The reaction of the dihalobenzenoid compound with the alkali metal salt of the dihydric phenol readily proceeds without need of an added catalyst upon the application of heat to such a mixture in the selected sulfone or sulfoxide solvent. 10

15 While the reaction temperature is not narrowly critical, it has been found that at temperatures below about room temperature, the reaction time is inordinately long in order to secure high molecular weights. The higher temperatures i.e. above room temperature and generally above 100°C., are much more preferred for shorter processing times and for a more economical system. Most preferred are temperatures between about 120°C. to 160°C. Higher temperatures can of course be employed, if desired, provided that care is taken to prevent degradation or decomposition of the reactants, the polymer and the solvents employed. 15

20 Also temperatures higher than 100°C. are preferred in order to keep the polymer in solution during the reaction since these sulfoxide and sulfone solvents are not particularly good solvents for the polymer except in the hot condition. It is a feature of this process that high molecular weights are possible only when the growing polymer chain is dissolved in the solvent. Once the polymer precipitates from the solvent, its growing ceases, although it has also been found that when this happens, the addition of a second cosolvent as hereinbefore mentioned to the reaction or by increasing the reaction temperature, the precipitated polymer can be redissolved and the polymerization continued to higher molecular weights. Among such other cosolvents as might be mentioned for use solely to increase the fluidity of the reaction mass are diphenyl ether, anisole, xylene, chlorobenzene and dichlorobenzene even though other azeotrope formers may have previously been used or are still in the reaction mass. 20

25 The reaction temperature can be effectively increased even above the normal boiling point of the solvent or mixture of solvents by the use of pressure in the reaction vessel. However, atmospheric pressures are quite adequate, though if desired pressures as high as 1000 psig. or more can be employed. 25

30 Preferably the polymerization reaction mass is a true solution at the reaction temperature except for by-product inorganic salt which is generally insoluble in the reaction mass. However, the reaction can still proceed as a swollen gel of solvent and dissolved polymer if high solids reaction conditions are desired. Equal parts by weight of reaction solvent and of total monomer reactants (based on the weight of sulfoxide or sulfone reaction solvent, exclusive of the azeotrope former, and total monomer reactants) seem to give optimum results. However, if adequate stirring is provided and means are available for stripping the solvent from the polymer mass are provided, as little as one part reaction solvent to five or more parts total monomer reactants can still be desirable. 30

35 If, however, the polymer precipitates from the solvent at the reaction temperature, and such polymer is found to be of sufficiently high molecular weight for the intended end use, the reaction mass can be actually a mixture of the solvent having the reactants dissolved therein and the precipitated polymer. 35

40 The polymer is recovered from the reaction mass in any convenient manner, such as by precipitation induced by cooling the reaction mass or by adding a nonsolvent for the polymer, or the solid polymer can be recovered by stripping off the solvent at reduced pressures or elevated temperatures. 40

45 Molecular weight of the polymer can be easily controlled by the addition of a precipitating solvent to the reaction mixture when the desired reduced viscosity of the resin is secured or when the indicated viscosity of the polymerization mass is high enough to indicate the desired molecular weights are achieved. It is also possible to terminate the growing polymer chain by the addition of a monofunctional chain stopper, e.g. an alkyl halide or other suitable coreactant. 45

50 Since the polymerization reaction results in the formation of the alkali metal halide on each coupling reaction, it is preferred either to filter the salts from the polymer solution or to wash the polymer to substantially free it from these salts. 50

55 The residue E in the above formula —O—E—O—E'— of the dihydric phenol can be, for instance, a mononuclear phenylene group as results from hydroquinone and 55

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resorcinol, or it may be a di- or polynuclear residuum. The residuum E can also be substituted with other inert nuclear substituents e.g. halogen, alkyl and alkoxy.

It is preferred that the dihydric phenol be a weakly acidic dinuclear phenol, for example, the dihydroxy alkanes or the nuclear halogenated derivatives thereof, which are commonly known as "bisphenols", for example, 2,2-bis-(4-hydroxyphenyl)propane. Other suitable dinuclear dihydric phenols are the bisphenols of a symmetrical or unsymmetrical joining group as for example, either oxygen ($-\text{O}-$), carbonyl ($-\text{CO}-$), sulfide ($-\text{S}-$), sulfone ($-\text{SO}_2-$), or hydrocarbon residue in which the two phenolic nuclei are joined to the same or different carbon atoms of the residue, for example, the bisphenol of acetophenone, the bisphenol of benzophenone, the bisphenol of vinyl cyclohexene, the bisphenol of a-penene, and other bisphenols where the hydroxyphenyl groups are bound to the same or different carbon atoms of an organic linking group.

Examples of specific dihydric polynuclear phenols include among others: the bis-(hydroxyphenyl)alkanes e.g. 2,2-bis-(4-hydroxyphenyl)propane, 1,2-bis-(4-hydroxyphenyl)ethane, 2,2-bis-(2-isopropyl-4-hydroxyphenyl)propane and 3,3-bis-(4-hydroxyphenyl)pentane; di(hydroxyphenyl)sulfones e.g. bis-(4-hydroxyphenyl)sulfone and, 5'-chloro-4,4'-dihydroxydiphenyl sulfone, di(hydroxyphenyl)ethers e.g. bis-(4-hydroxyphenyl)ether, the 4,3', 4,2', 2,2', 2,3'-dihydroxydiphenyl ethers, bis-(4-hydroxy-3-chloronaphthyl)ether and 4,4'-dihydroxy-2,5-diethoxydiphenyl ether.

It is also contemplated to use a mixture of two or more different dihydric phenols to accomplish the same ends as above. Thus when referred to above the E residuum in the polymer structure can actually be the same or different aromatic residua.

As used herein, the E term defined as being the "residuum of the dihydric phenol" refers to the residue of the dihydric phenol after the removal of the two aromatic hydroxyl groups. Thus it is readily seen that polyarylene polyethers contain recurring groups of the residuum of the dihydric phenol and the residuum of the benzenoid compound bonded through aromatic ether oxygen atoms.

The residuum E' in the above formula $-\text{O}-\text{E}-\text{O}-\text{E}'-$ of the benzenoid compound can be from any dihalobenzenoid compound or mixture of dihalobenzenoid compounds which compound or compounds have the two halogens bonded to benzene rings having an electron withdrawing group in at least one of the positions ortho and para to the halogen group. The dihalobenzenoid compound can be either mononuclear where the halogens are attached to the same benzenoid ring or polynuclear where they are attached to different benzenoid rings, as long as there is the activating electron withdrawing group in the ortho or para position of that benzenoid nucleus.

Any electron withdrawing group can be employed as the activator group in the dihalobenzenoid compound. Preferred are the strong activating groups e.g. the sulfone group ($-\text{SO}_2-$) bonding two halogen substituted benzenoid nuclei. It is further preferred that the ring contain no electron supplying groups on the same benzenoid nucleus as the halogen; however, the presence of other groups on the nucleus or in the residuum of the compound can be tolerated. Preferably, all of the substituents on the benzenoid nucleus are either hydrogen (zero electron withdrawing), or other groups having a positive sigma* value, as set forth in J. F. Bunnett in *Chem. Rev.*, 49, 273 (1951) and *Quart. Rev.*, 12, 1 (1958).

The electron withdrawing group of the dihalobenzenoid compound can function either through the resonance of the aromatic ring, as indicated by those groups having a high sigma* value, i.e. above about +0.7 or by induction as in perfluoro compounds and like electron sinks.

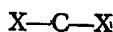
Preferably the activating group should have a high sigma* value, preferably above 1.0, although sufficient activity is evidenced in those groups having a sigma* value above 0.7.

The activating group can be basically either of two types:

(a) monovalent groups that activate one or more halogens on the same ring as a nitro group, phenylsulfone, or alkylsulfone, cyano, trifluoromethyl, nitroso, and hetero nitrogen as in pyridine;

(b) divalent groups which can activate displacement of halogens on two different rings, e.g. sulfone group $-\text{SO}_2-$; the carbonyl group $-\text{CO}-$; the vinyl group $-\text{CH}=\text{CH}-$; the sulfoxide group $-\text{SO}-$; the azo group $-\text{N}=\text{N}-$; the saturated

fluorocarbon groups $-\text{CF}_2\text{CF}_2-$; organic phosphine oxides $-\text{P}(=\text{O})(\text{R})_2-$; where R is a



hydrocarbon group, and the ethylidene group $-\text{C}-$ where X can be hydrogen, or halogen or which can activate halogens on the same ring such as with difluorobenzoquinone, 1,4- or 1,5- or 1,8-difluoroanthraquinone.

If desired, the polymers may be made with mixtures of two or more dihalobenzenoid compounds each of which has this structure, and which may have different electron withdrawing groups. Thus the E' residuum of the benzenoid compounds in the polymer structure may be the same or different.

It is seen that as used herein, the E' term defined as being the "residuum of the benzenoid compound" refers to the aromatic or benzenoid residue of the compound after the removal of the halogen atoms on the benzenoid nucleus.

The following examples are intended further to illustrate the present invention.

Reduced viscosity of the polyarylene polyethers (RV) was determined by dissolving a 0.2 gram sample of thermoplastic polyarylene polyether in a selected solvent contained in a 100 ml volumetric flask so that the resultant solution measured exactly 100 ml at 25°C. in a constant temperature bath. The viscosity of 3 ml of the solution which had been filtered through a sintered glass funnel was determined in an Ostwald or similar type viscometer at 25°C. Reduced viscosity values were obtained from the equation:

$$\text{Reduced Viscosity} = \frac{t_s - t_0}{c \cdot t_0}$$

wherein:

t_0 is the efflux time of the pure solvent

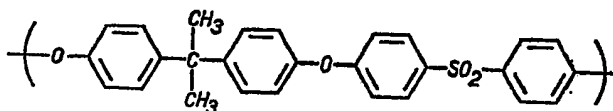
t_s is the efflux time of the polymer solution

c is the concentration of the polymer solution expressed in terms of grams of polymer per 100 ml of solution.

All parts and percentages are by weight unless indicated otherwise.

EXAMPLE 1

Into an air-free 500 ml flask equipped with a stirrer, gas inlet tube, thermocouple, distillation trap and reflux condenser was placed 65 grams of dimethylsulfoxide and 200 grams of chlorobenzene azeotrope former. The ratio of dimethylsulfoxide to chlorobenzene was 1:3.1. 30.0 Grams (0.1314 mole) of bisphenol A and 37.7 grams (0.1314 mole) of 4,4'-dichlorodiphenylsulfone were then simultaneously charged into the reaction flask which was immediately sparged with nitrogen to exclude any possibility of air contamination. Thereafter, the clear, nearly colorless solution was heated to about 75°C and 21.5 grams (0.2628 mole) of 49% aqueous sodium hydroxide were added from a dropping funnel. Two liquid phases formed immediately. The reaction mass was then heated to 120°C at which point a water-chlorobenzene azeotrope began distilling from the mixture. Distillation of the azeotrope was continued for about 30 minutes with a gradual rise in temperature to 140°C. at which point essentially all of the water in the mixture was removed. The disodium salt of bisphenol A precipitated and one liquid phase was present. Excess chlorobenzene was then removed by increasing the temperature gradually to about 170°C and distilling off excess azeotrope former for about 20 minutes. At this point the ratio of dimethylsulfoxide to chlorobenzene was 4:1. As soon as this ratio was reached, considerable polymerization occurs because of the high reaction temperature. The temperature of the reaction mass was rapidly dropped to about 150—160°C and held there with stirring for about one hour. Gaseous methyl chloride was introduced until no more was absorbed. The mixture was diluted to 10—15% solids by adding chlorobenzene. The polymer was isolated by coagulation in 4 volumes of ethanol after filtering to remove by-product sodium chloride. The finely divided white polymer was then dried in a vacuum oven at 110°C for 16 hours. The yield was 52 grams (90%) and the reaction was 100% complete based on a titration for residual base. The isolated polymer had a reduced viscosity in chloroform of 0.90, a very light amber color and was composed of recurring units having the formula:



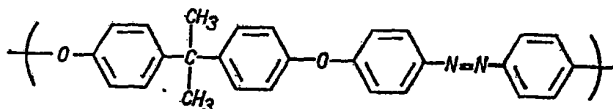
The total preparation time exclusive of polymer recovery and drying in this example was 1 hour, 50 minutes.

EXAMPLE 2

Example 1 is duplicated, but instead of converting bisphenol A *in situ* to the disodium salt, the disodium hexahydrate salt of bisphenol A is employed. Reaction time and polymer properties are comparable to those of Example 1.

EXAMPLE 3

Example 1 was duplicated except that in place of 4,4'-dichlorodiphenylsulfone, 32.0 g (0.1314 mole) of 4,4'-dichloroazobenzene was used. The isolated polymer had a reduced viscosity in p-chlorophenol of 0.17, a bright orange color owing to the presence of the azo linkages and was composed of recurring units having the formula:



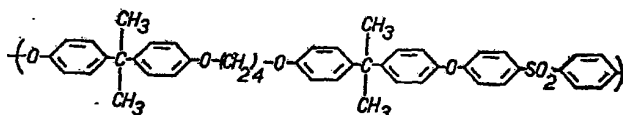
The preparation time for this example exclusive of polymer recovery and drying was 7 hours.

EXAMPLE 4

Example 1 was duplicated except that in place of 4,4'-dichlorodiphenylsulfone, 29.6 g (0.1314 mole) of 4,4'-difluoroazobenzene was used. Owing to the high reactivity of this monomer, polymerization was virtually complete at the conclusion of chlorobenzene removal. Upon cooling, the polymer separated from the viscous mass. It was estimated that the reduced viscosity was about 1, as measured in o-dichlorobenzene at 25°C, at this point. To reach this viscosity only an 18 minute reaction was required. Additional heating at 140—170°C over a 6½ hour period raised the reduced viscosity to 1.47. During this period most of the polymer appeared to be insoluble. The bright red polymer which was isolated was of the same structure as the product in Example 5. The total preparation time for this example exclusive of polymer recovery and drying was 8 hours.

EXAMPLE 5

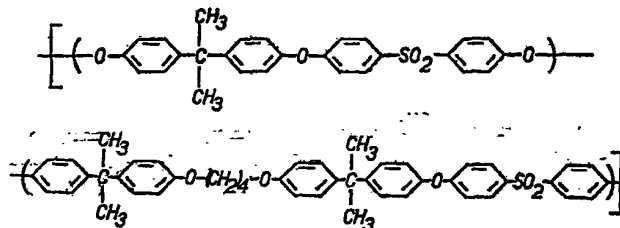
Example 1 was duplicated except that in place of bisphenol A, 25.5 g (0.05 mole) of tetramethylene dibisphenol A (the bisphenol prepared by condensation of 2 moles of p-isopropenyl phenol with 1,4-diphenoxybutane) and the corresponding molecular quantities of the 4,4'-dichlorodiphenyl sulfone (14.4 g, 0.05 mole) and caustic soda (8.1 g of 12.46 me/g., 0.10 mole) were used. The isolated polymer had a reduced viscosity as measured in chloroform of 0.80 and was composed of recurring units having the formula:



The total preparation time for this example, exclusive of polymer recovery and drying was 2 hours.

EXAMPLE 6

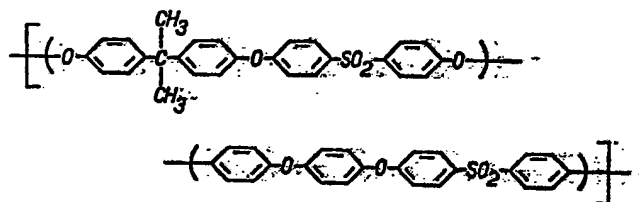
Example 1 was duplicated except that 22.5 g (0.0985 mole) of bisphenol A and 16.8 g (0.0329 mole) of tetramethylene dibisphenol A were used. The isolated polymer had a reduced viscosity of 0.85 as measured in chloroform and was composed of recurring units having the formula:



The total preparation time for this example exclusive of polymer recovery and drying was 2 hours.

EXAMPLE 7

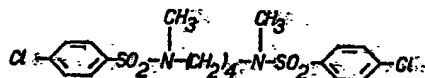
- 5 Example 1 was duplicated except that 22.5 g (0.0985 mole) of bisphenol A and 6.7 g (0.033 mole) of 4,4'-dihydroxydiphenyl ether were used. The isolated polymer had a reduced viscosity of 0.84 as measured in chloroform and was composed of recurring units having the formula:



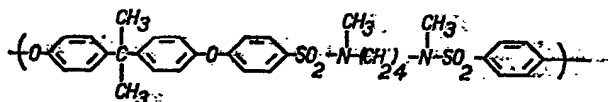
- 10 The total preparation time for this example exclusive of polymer recovery and drying was 2 hours.

EXAMPLE 8

Example 1 was duplicated except that in place of 4,4'-dichlorodiphenylsulfone, 61.17 g of 1,4-bis-(*p*-chloro-*N*-methyl-benzenesulfonamido)butane, having the formula



- 15 (melting point 179.5—180.5°C) and prepared by the reaction of potassium *p*-chloro-*N*-methyl-benzenesulfonamide with 1,4-dichlorobutane, was used, and the reaction time was 2 hours at about 160°C. The isolated polymer had a reduced viscosity in chloroform at 25°C of 0.85. The polymer was composed of recurring units having the formula:

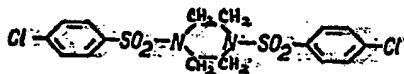


A film molded at 220°C exhibited the following properties:

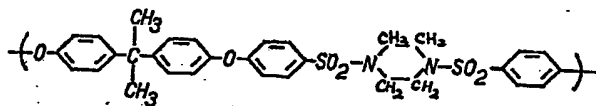
25.	Tensile Modulus	275,000 psi
	Tensile Strength	8,000 psi
	Elongation	6%
	Pendulum Impact	55 ft.lb./in.

EXAMPLE 9

Example 1 was duplicated except that in place of 4,4'-dichlorodiphenylsulfone, 57.2 g of piperazine bis-*p*-chlorobenzenesulfonamide having the formula:



- 30 (melting point 324—325°C) and prepared by reacting *p*-chlorobenzenesulfonyl chloride with piperazine, was used. The polymerization time was 1 hour at 160—170°C. The polymer crystallized out on cooling the reaction mixture and exhibited a melting point of 255—260°C and an RV in *p*-chlorophenol at 47°C of 0.84. The polymer was composed of recurring units having the formula:



A pressed film had a tensile modulus of 350,000 psi.

WHAT WE CLAIM IS:—

1. A process for the preparation of substantially linear thermoplastic polyarylene polyethers which process comprises (a) simultaneously contacting substantially equimolar amounts of an alkali metal double salt of a dihydric phenol and a dihalobenzenoid compound having an inert electron withdrawing group in at least one of the positions ortho and para to the halogen atom, with a solvent mixture comprising an azeotrope former and an organic reaction solvent having the formula:



wherein R is a hydrocarbon group free of aliphatic unsaturation, on the alpha carbon atom, and contains less than 8 carbon atoms, or wherein the two R groups are connected together as a divalent alkylene group, and wherein z is 1 or 2, the azeotrope former and the organic reaction solvent being present in a weight ratio of from 10:1 to 1:1 (b) removing water from the reaction mass as an azeotrope with said azeotrope former until substantially anhydrous conditions are attained, (c) removing excess azeotrope former until the ratio of said azeotrope former to said reaction solvent is from 1:1 to 1:10, and (d) reacting said alkali metal double salt with said dihalobenzenoid compound in the liquid phase of said reaction solvent.

2. A process as claimed in claim 1 wherein the initial weight ratio of the azeotrope former to the organic reaction solvent is from 4:1 to 3:1.

3. A process as claimed in claim 1 or claim 2 wherein the weight ratio of the azeotrope former to the organic reaction solvent after removal of excess azeotrope is from 1:3 to 1:4.

4. A process as claimed in any one of the preceding claims wherein oxygen is excluded from the reaction mass.

5. A process as claimed in any one of the preceding claims wherein the organic reaction solvent is dimethyl sulfone, diisopropylsulfone, diphenyl sulfone, tetrahydrothiophene 1,1-dioxide, or tetrahydrothiophene-1 monoxide.

6. A process as claimed in any one of claims 1 to 4 wherein the organic reaction solvent is dimethylsulfoxide.

7. A process as claimed in any one of the preceding claims wherein the water content of the reaction mass is reduced to less than 0.5 per cent by weight.

8. A process as claimed in any one of the preceding claims wherein the azeotrope former is benzene, xylene, or a halogenated benzene.

9. A process as claimed in any one of the preceding claims wherein the water is removed as an azeotrope by heating at reflux.

10. A process as claimed in any one of the preceding claims wherein the alkali metal double salt is hydrated.

11. A process as claimed in any one of the preceding claims wherein the reaction is conducted at a temperature above 100°C. and below the decomposition temperature of the reactants, the azeotrope former, the reaction solvent and the polymer formed.

12. A process as claimed in any one of the preceding claims wherein the dihydric phenol from which the alkali metal double salt is derived is a bisphenol.

13. A process as claimed in claim 12 wherein the bisphenol is 2,2-bis-(4-hydroxyphenyl)propane.

14. A process as claimed in any one of claims 1 to 11 wherein the dihydric phenol from which the alkali metal double salt is derived is a dinuclear phenol in which the nuclei are joined by an oxygen, carbonyl, sulfide or sulfone linkage, or by a hydrocarbon residue.

15. A process as claimed in any one of the preceding claims wherein the dihalobenzenoid compound is a dinuclear benzenoid compound in which the nuclei are linked by the said electron withdrawing group.

16. A process as claimed in claim 15 wherein the electron withdrawing group is a sulfone group.

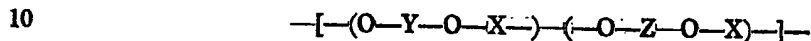
17. A process as claimed in any one of the preceding claims wherein the alkali

metal double salt of a dihydric phenol is formed *in situ* by reacting the dihydric phenol with a substantially stoichiometric amount of an alkali metal, or an alkali metal hydride, hydroxide, alkoxide or alkyl.

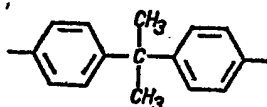
18. A process for the preparation of substantially linear thermoplastic polyarylene polyethers substantially as hereinbefore described in any one of the Examples.

19. Thermoplastic polyarylene polyethers when prepared by a process as claimed in any one of the preceding claims.

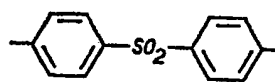
20. A substantially linear thermoplastic polyarylene polyether composed of recurring units having the formula:—



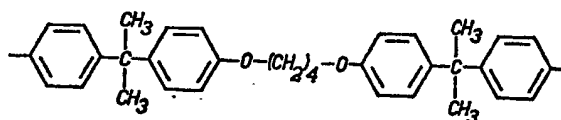
wherein: Y is



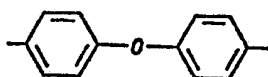
X is



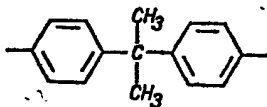
and Z is



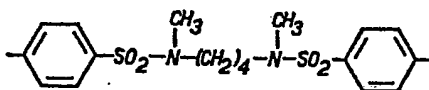
or



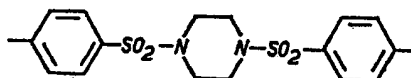
or Y and Z are the same and are



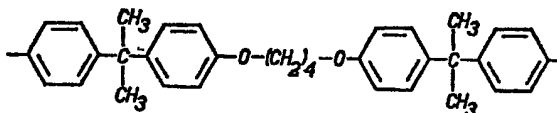
and X is



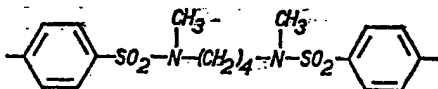
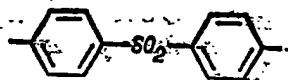
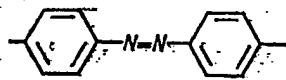
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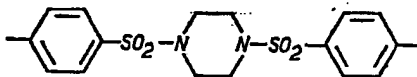
or Y and Z are the same and are



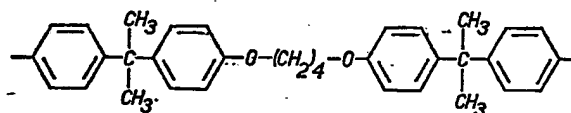
and X is



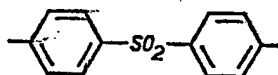
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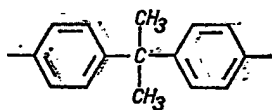
21. A polyether as claimed in claim 20 wherein Y and Z are:



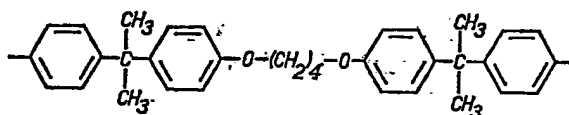
and X is



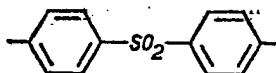
22. A polyether as claimed in claim 20 wherein Y is:



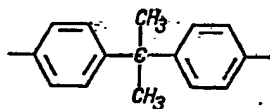
Z is



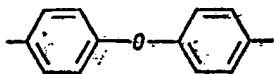
and X is



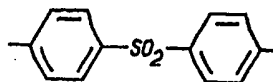
23. A polyether as claimed in claim 20 wherein Y is:



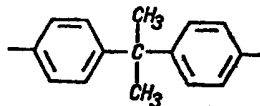
Z is



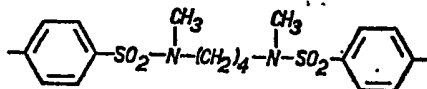
and X is



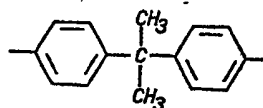
24. A polyether as claimed in claim 20 wherein Y and Z are:



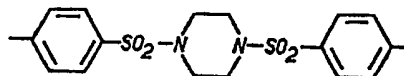
and X is:



25. A polyether as claimed in claim 20 wherein Y and Z are:



and X is:



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